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Magnetic Characterization of Organic Materials

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Magnetic Characterization of Organic Materials

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Abstract

Organic materials show interesting phenomena called magnetic field effects (MFEs), modulating their photophysical and electrical properties such as resistance and electro/photoluminescence by external magnetic field. Also, these attractive phenomena can be applied to magneto-optic or magneto-electric devices allowing us to control the functionalities of organic devices (OLED, OPV, OFET) with applied magnetic field. In this regard, we have a plan to investigate MFEs on the behaviors of charge/spin carriers in organic materials, such as charge mobilities, charge transfer, trapping, charge separation and recombination by **magnetic field applied spectroscopic** methodologies.

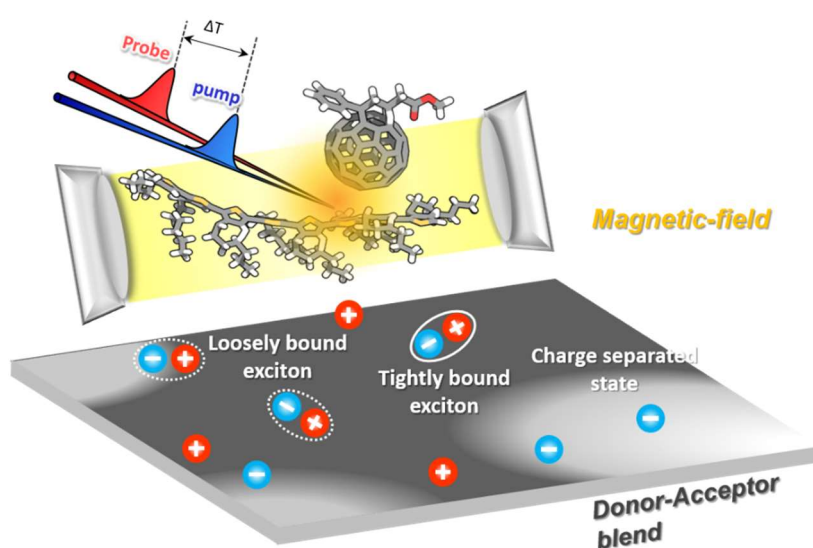


Figure 1. Various applications of magneto- optic and electric devices

Introduction

Recently, magnetic phenomena of organic materials have been extensively studied for both fundamental and technological reasons. Especially, organic materials show the distinctive features that low magnetic field, below ~ 100 mT, affects their electrical and photophysical properties, which has not been observed in conventional magnetic materials. These features can be applied to various organic devices (OLED, OPV, OFET), which allows us to magnetically modulate their properties, such as quantum yields, diffusion lengths, and charge mobilities. In this context, a detailed understanding of magnetic features is crucial to develop novel magneto-optic or magneto-electric organic devices.

In this project entitled “magnetic characterization of organic materials”, we will focus on exploring the magnetic field dependent photophysical properties, such as magneto-photoluminescence (MPL), magneto-photo induced absorbance (MPA) and their time-dependent features. As the photophysical data represent the transition and population of charge/spin carriers at specific energy levels, the carrier dynamics under magnetic field can be elucidated by spectroscopic measurements. For this purpose, various electromagnet-integrated spectroscopic tools will be developed, and delicate modification of organic materials will also be conducted to maximize their magnetic properties, which includes a development of synthetic strategies for organic molecules, their derivatives and nanostructures, such as molecule complexes, supramolecular assemblies, and

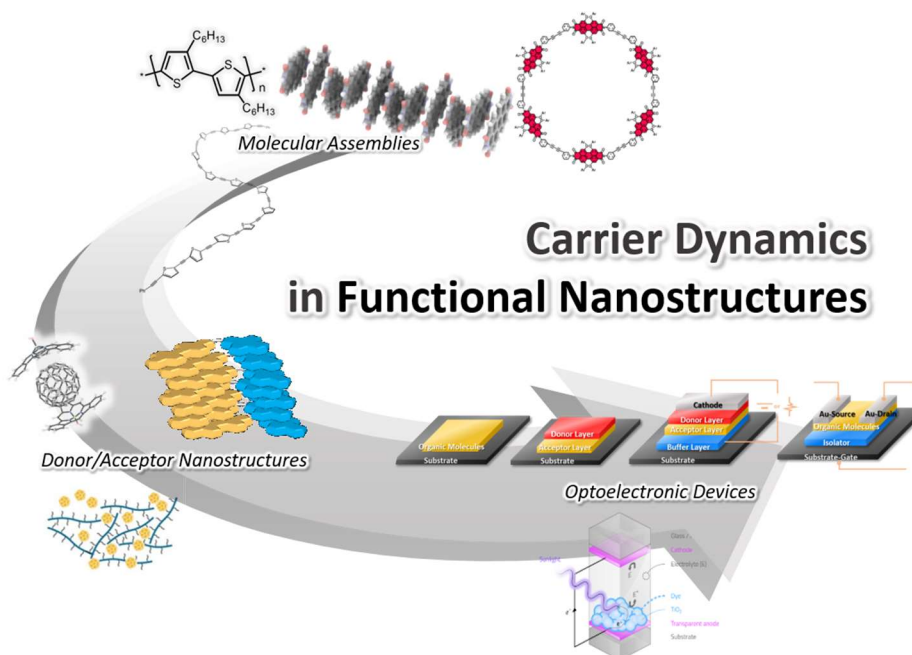


Figure 1. Examples of samples, nanostructure, and their devices

heterojunctions.

The spectroscopic characterization will provide an opportunity to understand the fundamental mechanism of MFE, which could give a clue to addressing a number of certain practical goals, namely how to control the performances of OLEDs, OPVs, OFETs, and lasers. Given this expectation, we believe that our research on magnetic characterization of organic materials will translate into innovative developments that not only allow the species/structure-magnetic property relationships to be probed in a greater detail, but also give rise to a number of real-world applications. Consequently, with a development of reliable magnetic characterizing apparatus and a delicate tuning of the species and structures of organic materials, we will explore the fundamental mechanism of MFE in various organic materials, and their complexes and devices.

Experimental

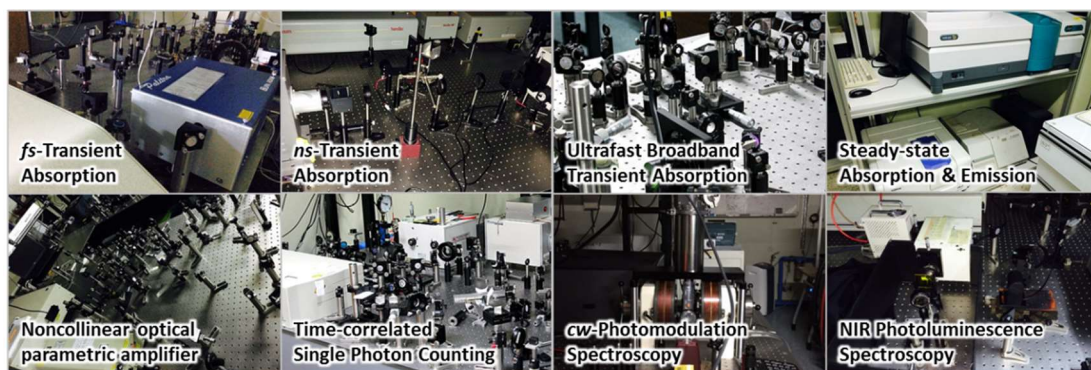


Figure 3. Instruments of steady-state and time-resolved spectroscopy

I. Experimental methods

1. Steady-state Spectroscopy

- UV-Vis-NIR Absorption & Emission Steady-state Spectroscopy
- NIR Photoluminescence Spectroscopy
- *cw*-Photomodulation Spectroscopy

2. Time-Resolved Laser Spectroscopy

- Time-Correlated Single Photon Counting Technique
- Nanosecond Transient Absorption Spectroscopy
- Femtosecond Transient Absorption Spectroscopy
- Ultrafast Broadband Transient Absorption Spectroscopy

II. Quantum Mechanical Calculation

- Quantum Mechanical Calculations
 - : Density functional theory calculations with Gaussian and Dalton
- Molecular Dynamics Simulations
 - : Molecular dynamics simulations with NAMD

Results and Discussion

I. Instrument

Magnetic-field Applied Low Temperature *cw*-Photomodulation Spectroscopy

The last decade has reached a consensus that the behaviors of photo-generated species play crucial roles in the performances of organic based optoelectronic devices such as organic field effect transistors (OFETs) and organic solar cells (OSCs). Especially, formed by dissociation processes of excitons, weakly-bound excitons and free polarons contribute directly to the efficiency of photocurrent and energy conversion in organic devices. Vigorous research activities on material science have reported that such charge species in organic materials exhibit excited-state lifetimes ranging from sub-micro seconds to milliseconds. Thus, unveiling the behaviors of charge species under the magnetic field will pave a way to find out correlations with device performances.

In our project, we have introduced *cw*-photomodulation (PM) spectroscopy to investigate the nature of photo-generated species, especially charge-transfer excitons and free polarons. Using this technique, the charge species with a lifetime from sub-micro seconds to milliseconds have dominantly been investigated by mechanical modulation achieved by an optical chopper. In addition, a broad wavelength coverage from visible to near-infrared was utilized for PM spectroscopy, because excited-state absorption of charge species such as charge-transfer excitons and free polarons appears in low energy region; in polyphenylene vinylene (PPV), for example, excited-state absorption of exciton appears around 600~800 nm, while that of polaron appears around 800~1100 nm. Our electromagnet was custom-designed (C-shaped) and installed for PM spectroscopy to apply magnetic field up to 500 mT with high uniformity. Pump and probe beams of PM setup were focused and

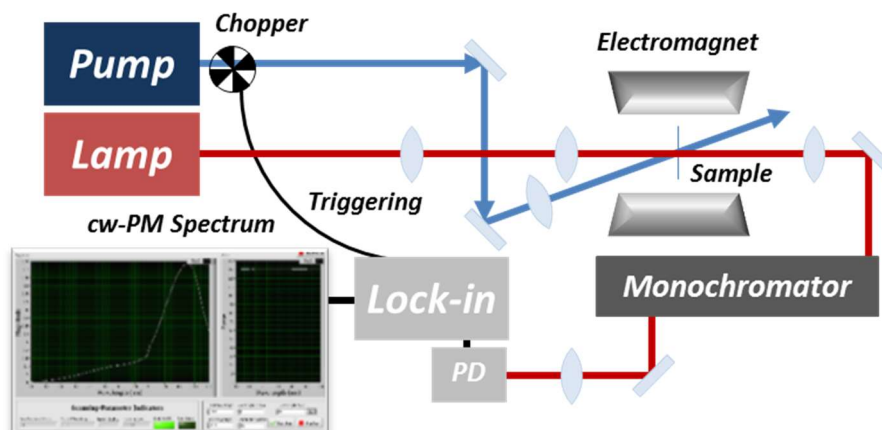


Figure 4. Scheme of magnetic-field applied *cw*-photomodulation spectroscopy

overlapped at the position between two magnetic poles in which the stability of magnetic-field was below 0.1 %.

As the PM spectra represent the accumulative excited-state feature of charge species, PM spectroscopy is a primary work for understanding the predominant effect of magnetic field on charge-transfer excitons and free polarons. Furthermore, the PM spectra provide valuable information on charge species; the spectral regions in which each excitonic/polaronic species are located. Hence, we have installed a setup, magnetic-field applied PM spectroscopy, and will develop magnetic-field applied time-resolved spectroscopic instruments which will be discussed further below.

For PM spectroscopy, the population of charge species is a key aspect for a high signal to noise ratio. At low temperature, the intersystem crossing and charge dissociation processes become favored over non-radiative recombination processes. In addition, to avoid quenching of triplet excitons and polarons which are sensitive to oxygen, high vacuum condition is requisite for the measurements of charge species. In our laboratory, to minimize the non-radiative recombination and quenching processes, the customized cryostat was introduced for PM measurements under 60 K and 10^{-3} Torr. Our low-temperature PM spectroscopic setup is an effective tool for characterizing charge species with a high signal to noise ratio.

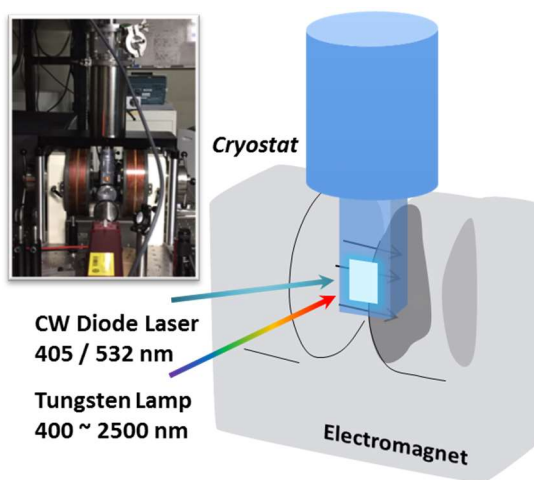


Figure 5. Customized cryostat and electromagnet for cw-PM spectroscopy

Magnetic-field applied Ultrafast Broadband Transient Absorption Spectroscopy Setup

One of the most widely utilized time-resolved spectroscopic techniques, transient absorption (TA) spectroscopy, allows scientists to observe various transient species (singlet/triplet excitons, charge-transfer states, and free polarons) and their evolutions over time. We have employed the TA spectroscopy to observe the overall dynamics of photo-generated species covering from generation to recombination processes, which directly contributes to performances of the organic devices. Thus, the TA spectroscopy is a powerful tool for studying the underlying mechanisms in the function of organic devices. To investigate the dynamics of photo-generated species in organic materials, we have developed ultrafast broadband TA spectroscopy which is superior to conventional setups in terms of

two following reasons: 1) improved time resolution (~ 50 fs) and 2) broad spectral range of probe pulses (300 \sim 1700 nm).

Introduction of pulse compression technique enhanced the time resolution of our TA instrument (50 fs) by utilizing a chirped mirror pair to modulate pulse widths. Moreover, as a probe beam, a light pulse that covers the visible wavelength region was previously utilized, and now the probe wavelength has been extended to near-IR region in which charge-transfer states and free polarons are located. In our laboratory, PPSLT (periodically-poled stoichiometric lithium tantalate) crystal was utilized to generate NIR probe pulse from 1100 to 1700 nm region with a high stability. Our established ultrafast broadband TA spectroscopic setup will be utilized to study various organic materials.

A sample chamber for degassing and argon purging has been designed and installed. As mentioned above, the inert condition is requisite for investigating charge dynamics in organic materials, which reduces a possibility of sample degradation under laser irradiation and exposure to

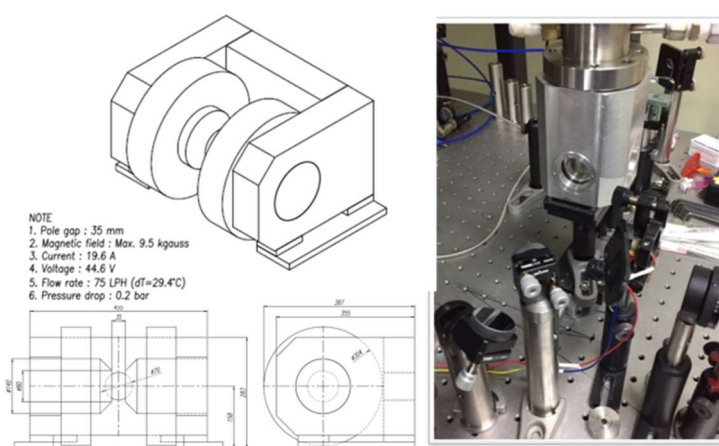


Figure 6. Customized electromagnet and chamber for ultrafast Transient absorption spectroscopy

oxygen. Furthermore, an electromagnet has been designed to apply magnetic field up to 1 T for ultrafast broadband TA spectroscopic measurements. Magnetic shielding of nearby optical components was achieved for reliable experimental results. Magnetic-field applied ultrafast broadband TA setup will be completed in the near future.

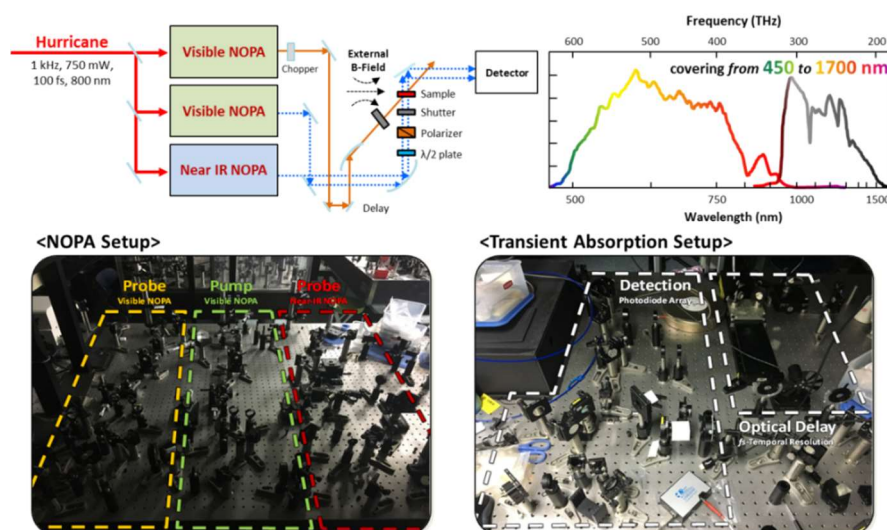


Figure 7. Scheme of Ultrafast Broadband Transient Absorption Spectroscopy

II. Materials & Nanostructures

Rosarin Derivative/Fullerene Complex as Organic Donor/Acceptor System

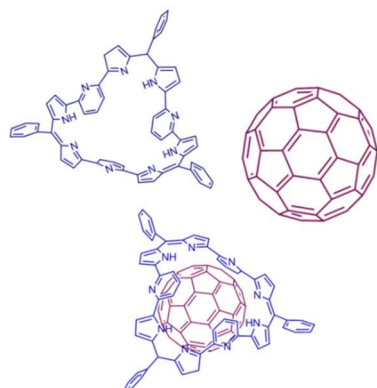


Figure 8. Molecular structures of rosarin derivative, C₆₀ and the complex

In our project, the magnetic features of a simple organic donor/acceptor system have been elucidated. As a starting material, rosarin derivative/ fullerene complex was considered because of its stoichiometric binding behavior (rosarin derivative: fullerene 1:1 or 2:1). From X-ray structures expanded rosarin derivative exhibits dome-shaped structure which is prone to capture ball-shaped fullerene molecules. In this complex, rosarin

derivative behaves as an efficient electron donor and fullerene acts as an electron acceptor, respectively. In the excited-state of the complex, ultrafast charge separation was observed and charge transfer state was efficiently generated. In this regard, PM and ultrafast broadband TA spectra were recorded for rosarin derivative/fullerene complex.

PM Measurements on Rosarin Derivative/Fullerene Complex and Magnetic Field Effects

The PM technique was employed to investigate the organic rosarin derivative/ fullerene complex. Through encapsulating half of the bucky-ball, C₆₀ by dome-shaped rosarin derivative, rosarin derivative/fullerene complex was formed by π - π interaction. Upon excitation of rosarin derivative/fullerene complex, electron transfer occurs from rosarin to fullerene in the excited-state. Based on electron transfer processes generating hole at rosarin derivative and electron at fullerene, electrostatically bounded charge-transfer state was developed which finally evolves into triplet excited-state of rosarin derivative via charge recombination.

In the excited-state of rosarin derivative/fullerene complex, two photo-generated species were generated; charge-transfer state of rosarin derivative/fullerene complex and triplet excited-state of rosarin derivative. In the PM spectrum, two spectral features appeared; excited-state absorption of C₆₀ anion at 1080 nm and that of triplet excited-state of rosarin derivative at 780 nm. The excited-state absorption band of C₆₀ anion at 1080 nm is relatively weak in magnitude in comparison with that of triplet excited-state of rosarin derivative at 780 nm because the PM spectrum reflects time-averaged features of excited-state; shorter lifetime of charge-transfer state compared to that of triplet excited-state of rosarin derivative.

Zeeman splitting induced by external magnetic field lifts the degeneracy of spin-states. Energetics of spin sublevels are influenced by the magnitude of external magnetic field and the relative orientation between external magnetic field vector and net spin angular momentum vector of correlated electrons. Generally, in organic donor/acceptor system, singlet and triplet spin configurations of charge-transfer state, also called radical-pair intermediate, are energetically degenerate. In the case of rosarin derivative/fullerene complex, however, exchange interaction is not negligible. Rosarin derivative/fullerene complex, formed by π - π interaction, keeps in distance of several angstroms between the two molecules, thus, dipole-dipole interactions between two lone-pair electrons occupied in rosarin derivative and fullerene are expected. Therefore, singlet and triplet spin configurations of charge-transfer state of the complex are weakly separated by the exchange energy, $2J$. Applying external magnetic field, three sublevels of triplet charge-transfer state split into three distinctive spin states and a coherence between singlet/triplet charge transfer states is established at certain magnitude of external magnetic field when they become energetically degenerate. In our preliminary measurements, it was observed that enhanced coherence between singlet/triplet charge-transfer states occurs at 150 mT, resulting in an increase in the population of triplet excited-state of rosarin derivative and a decrease in C_{60} anion population from the PM spectra. This phenomenon derives from the altered spin-state of initially formed charge-transfer state, which is called indirect mechanism of magnetic field effect. As the final state via charge recombination process is the triplet excited-state of rosarin derivative, the initial state contains more triplet character, the more charge

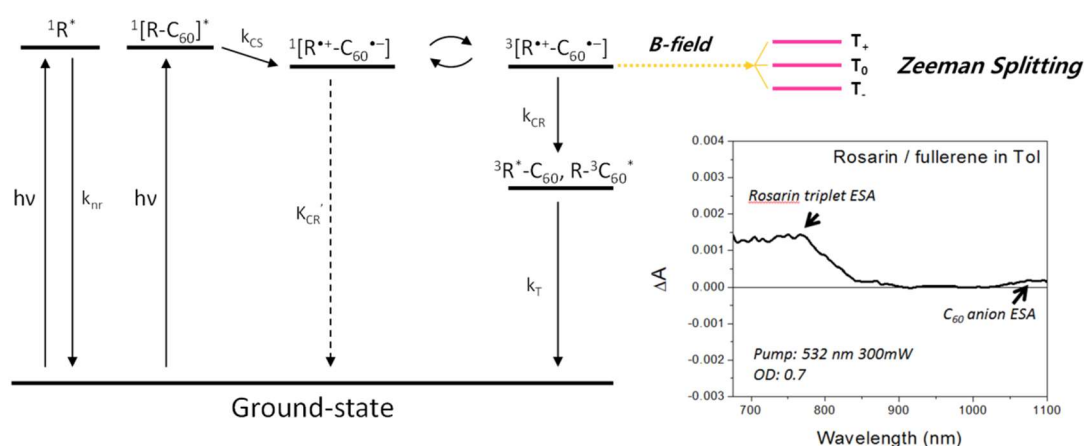


Figure 9. Schematic representation of excited-state dynamics of rosarin derivative/fullerene complex and cw-Photomodulation spectrum of the complex

recombination process occurs. Further experiments are expected to verify our hypothesis, for example, PM measurements varying the magnitude of external magnetic field. In addition, theoretical calculations will be introduced to evaluate the exchange interaction energy (J) to correlate with the magnetic energy induced by external magnetic field.

Ultrafast Broadband Transient Absorption Measurements of Rosarin Derivative/Fullerene Complex and Magnetic Field Effects

Expanded rosarin derivative is a dome-shaped molecule designed for complexation with C_{60} . With this expectation, solid crystals of 1:1 and 2:1 (rosarin derivative: C_{60}) complexes were obtained. From the titration experiments such as HNMR and UV/VIS absorption measurements, we can presume that the 1:1 complex is mainly formed in solution phase. To explore its excited-state dynamics, we carried out ultrafast broadband transient absorption measurements in spectral region from 350 to 1700 nm (only spectral region from 450 to 1200 nm was plotted where distinctive bands appear). C_{60} anion peak at 1075 nm strongly supports the formation of CT state in solution phase.

Upon photoexcitation, pristine rosarin derivative decays with 1.5 and 23 ps lifetimes, structural relaxation for the former and electronic relaxation for the latter, respectively. These two components appear in titrated sample of rosarin derivative with C_{60} (1 equivalent) and three additional components were detected with the lifetimes of less than 200 fs, 2.2 ns, and long residual. Since both the complex and pristine rosarin derivative are present, its excited-state dynamics is complicated. Neglecting the two components of pristine rosarin derivative mentioned earlier (1.5 and 23 ps), less than 200 fs component can be assigned as charge separation, 2.2 ns as charge-recombination process, and long residual as triplet state.

Since rosarin derivative/fullerene complex forms radical pair intermediate in the excited-state, spin configuration of its charge transfer state was modulated by external magnetic field. As discussed above, the triplet character of charge transfer state became enhanced under the external magnetic-field, which induces efficient charge recombination

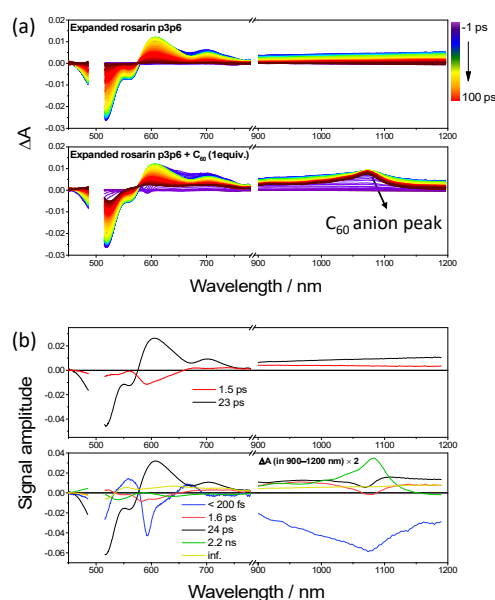


Figure 10. (a) Transient absorption spectra of rosarin derivative and the complex (b) Decay associated spectra of rosarin derivative and the complex.

that forms the triplet excited-state of rosarin derivative. Thus, the lifetime of charge transfer state is expected to be shortened. At the same time, the triplet excited-state features appear at earlier time domains in the TA spectrum.

Our ongoing magnetic-field effect study on rosarin derivative/fullerene complex gives valuable insights into charge recombination dynamics, which will strengthen the basis of organic spintronics research.

Collaborative Work with Prof. Persoon

Investigations on Magnetic Properties of π -conjugated Organic Nanorings

Over the past decade nanomaterials have been an important issue in the field of material science. Researchers have mainly focused on inorganic materials such as nanocrystals and quantum dots to study their superior optical properties for energy and photovoltaic devices. Recently, however, growing interest in the synthesis and characterization of organic nanorings has been witnessed. Attributed to their novel optical/magnetic properties such as Faraday rotation and ferromagnetic hysteric behaviors, organic nanorings are referred to as quantum rings. In this manner, our collaborative research focuses on studying magnetic properties of π -conjugated organic nanorings composed of thiophene units.

Motivated by extremely strong Faraday rotation, nonlinear magneto-optic effect, and ferromagnetic hysteric behavior in highly regioregular polythiophene films, we spurred interests in investigating magnetic properties of polythiophenes. Interestingly, when external magnetic field is applied, we have observed that regioregular polythiophene nanorings sustain persistent currents resulting in large magnetic moments. Concomitantly nanosized doughnut structures ($\varnothing \sim 12$ nm) were observed in polythiophene films from AFM images. We propose that magnetic properties of organic nanorings are derived from their regioregular nanoring structure of polythiophenes.

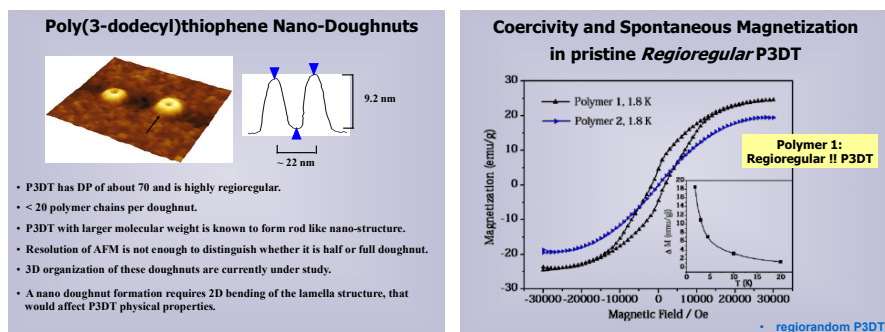


Figure 11. doughnut structure in thin films of poly(3-dodecylthiophene) and ferromagnetic transition at 1.8K in pristine regioregular poly(3-dodecylthiophene).

In this project, to investigate structural dependent magnetic properties such as their ring sizes of polythiophene macrocycles, we focused on the synthesis of various polythiophene nanorings to study their unique magnetic properties. Prior to synthesis, there have been extensive computational works on these macrocycles regarding its complexity. There are two aspects to be met for maintaining permanent currents around nanorings; (1) the length of organic nanorings which should be smaller than the phase coherence of electrons (2) defect-free cyclic structure of nanorings to maintain coherence. From the calculation results, it is required that the circumference of the ring should be smaller than the phase coherence length of the electron. Thus, nanorings should be composed of 10 to 20 monomers of thiophene with a circumference of 7 – 17 nm. Another requirement is the absence of defects in the nanoring which would result in localization of electron. The synthesis of a series of polythiophene nanorings is in progress based on the calculation results.

In Prof. Persoon's group, size-dependent magnetic properties of polythiophene nanorings will be investigated. In a collaborative manner, in our group, their conjugation lengths will be characterized by steady-state absorption and emission measurements. In addition, employing transient absorption measurements, photogenerated charge carrier dynamics in assemblies of polythiophene nanorings will be investigated and magnetic-field effects on charge carrier dynamics will be carried out further. Our collaborative research will pave a way to develop new organic materials with magnetic properties for nanotechnology applications.

Publication List

1. Radical and Diradical Formation in Naphthalene Diimides through Simple Chemical Oxidation

Sangsu Lee,^a Fang Miao,^b Hoa Phan,^b Tun Seng Heng,^c Jun Ding,^c Jishan Wu^{*b} and Dongho Kim^{*a}

Chem. Commun. **2016**. Submitted

2. Increased Efficiency of MAPbI₃ Perovskite Solar Cells through Singlet Fission Processes of TIPS-pentacene

Sangsu Lee, Daesub Hwang, Seok Il Jung and Dongho Kim*

J.Mater.Chem.A. **2016**. submitted